NEW DEVELOPMENTS IN MICRO ANALYTICAL CHEMISTRY

BY

WILLIAM HENRY TAYLOR

B.S., University of Wisconsin, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1941

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The problems studied in connection with this thesis were suggested by and carried out under the direction of Dr. G. F. Smith. Appreciation is expressed for this coöperation.

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INTRODUCTION

One of the noteworthy advances in chemistry has been the introduction of methods and techniques permitting chemical operations with smaller amounts of substances than commonly used, a fact well recognized in chemical research, both inorganic and organic. In certain branches of chemistry the application of micro methods has become a necessity, particularly in the field of hormones, vitamins, etc.

The three main purposes of the present work were:

1. To study the possibility of extending micro analytical chemistry to fields in which it has not as yet been extensively applied.
2. To study a number of the more common micro analytical methods in the hope of effecting modifications which would increase the accuracy, as well as extend the application, of the methods.
3. To introduce improvements in apparatus design.

PART I-A

In the standard Pregl method for the determination of carbon and hydrogen in pure organic compounds,[1] the compound is burned in a measured volume of oxygen under controlled pressure conditions to yield, quantitatively, carbon dioxide from the carbon and water from the hydrogen. The carbon dioxide and water thus produced are quantitatively absorbed by suitable absorption tubes containing appropriate absorbing agents.

A study was made to determine the possibility of using "mikohbite" — mica impregnated with potassium hydroxide — and mica impregnated with anhydrous magnesium perchlorate as absorbing agents for the carbon dioxide and water respectively. The advantages to be obtained in the use of these reagents instead of the standard reagents, which are "ascarite" — asbestos impregnated with sodium hydroxide — for carbon dioxide, and "anhydrone" —anhydrous magnesium perchlorate—for water, are as follows:

1. "Mikohbite" is much less expensive than "ascarite," and the use of potassium hydroxide rather than sodium hydroxide leads to a lower vapor pressure at the expense of a slight decrease in capacity. "Mikohbite" also gives a better indication of exhaustion than "ascarite."

Both of these methods give results within the experimental error expected of a micro Kjeldahl determination although the second method sacrifices a small degree of accuracy for increased speed.

PART III

To investigate the possibility of applying micro analytical technique to the schematic analysis of a silicate, a sample of the mineral, alunite, was subjected to a complete analysis, using standard methods and both macro and micro technique. The values obtained were in good agreement, thus indicating the reliability of the micro analysis.

At the same time a study was made in which a perchloric acid digestion was used to "open" the sample instead of the usual sodium carbonate fusion. This was found to be satisfactory in this particular case, and it seems quite possible that its use might be extended to the analysis of other types of silicates as well. It offers the advantage of eliminating the troublesome J. Lawrence Smith fusion [4] for the determination of sodium and potassium and thus enabling the determination of all bases using one sample only.

PART IV

This part of the investigation was concerned with a study of the preparation and the application of tetrasulfato potassium cerate as a standard of reference in micro cerimetry. The salt was prepared by the addition of a saturated solution of potassium sulfate to a sulfuric acid solution of either ceric sulfate or ceric oxide. After filtration of the resulting precipitate, the tetrasulfato potassium cerate was crystallized from the filtrate.

The stable form of the salt was found to be the dihydrate, and analysis showed a purity of 99.8 per cent without recrystallization. Drying at 110° C. resulted in conversion to the monohydrate, and at 150° C. in conversion to the anhydrous salt.

The application of tetrasulfato potassium cerate in micro cerimetry was studied by analysing various samples of pure potassium ferricyanide for per cent iron and comparing the results with those obtained by using a standard solution of hexanitrato ammonium cerate as oxidant.

PART V

With the development of methods of preparation of substituted o-phenanthroline compounds by Richter,[5] it seemed of interest to

examine the possibility of using the ferrous complexes of these reagents in micro qualitative and quantitative separations of anions. Accordingly a systematic semi-quantitative measurement of the solubilities of the complex salts formed by the addition of ferroin, 5-bromo ferroin, 5-chloro ferroin, 5-methyl ferroin, 5-nitro ferroin, and 5-methyl-6-nitro ferroin to solutions of a large number of anions was undertaken.

Measurements were made in which 0.01 N anion solutions and 0.01 N reagent solutions were mixed in equal proportions, then with 100 per cent excess anion solution, and finally with 100 per cent excess of reagent solution. The degree of solubility was determined by visual estimation of the color remaining in the solution after filtration.

Results obtained in this study indicate the possibility of a large number of separations warranting further investigation.

PART VI

Suggestions for extension of the work of a similar nature have been outlined.

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VITA

The author was born May 4, 1915, in Wausau, Wisconsin, and obtained his elementary and secondary education in the public schools of that city. In 1931 he entered Columbia College, Dubuque, Iowa, and attended that institution for one year. In 1932 he transferred to the University of Wisconsin and remained for one year. He spent the years 1933 to 1935 in the employ of the Marathon Chemical Company, Rothschild, Wisconsin, as assistant analytical chemist. In the fall of 1935 he reëntered the University of Wisconsin and received the B.S. degree in 1937.

He entered the graduate school of the University of Illinois in the fall of 1937 as an Assistant in Analytical Chemistry. He held this position for two years and in 1940 was an Assistant in Microchemistry. He was again an Assistant in Analytical Chemistry during the school year 1940-1941.

His publications are:

Smith, G. F., and Taylor, W. H., An Electric Heating Mortar, Ind. Eng. Chem., Anal. Ed., 13, 203 (1941).